

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
12 April 2001 (12.04.2001)

PCT

(10) International Publication Number
WO 01/25393 A1

(51) International Patent Classification⁷: **C11D 17/00**

(21) International Application Number: **PCT/US00/27300**

(22) International Filing Date: **4 October 2000 (04.10.2000)**

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:
9923393.4 5 October 1999 (05.10.1999) **GB**
9923344.7 5 October 1999 (05.10.1999) **GB**
0010599.9 3 May 2000 (03.05.2000) **GB**
0022529.2 13 September 2000 (13.09.2000) **GB**

(71) Applicant (for all designated States except US): **THE PROCTER & GAMBLE COMPANY** [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **MCGOFF, Matthew, Grady** [US/GB]; 3 Jesmond Park Mews, Jesmond Park West, Newcastle upon Tyne NE7 7BA (GB). **STEPHENS, Scott, Edward** [US/GB]; 25 Deneside Court, Newcastle upon Tyne NE2 1JW (GB). **TANTAWY, Hossam, Hassan** [GB/GB]; The Chimes Lodge, Fulbeck, Morpeth NE61 3JT (GB). **DRIFFIELD, Christopher, Charles** [GB/GB]; 12 Westlands, High Heaton, Newcastle upon Tyne NE7 7YN (GB). **CORRAND, Didier, Marcel** [FR/IT]; Via Mascarola, 40, I-65013 Citta Santa Angelo (IT).

(74) Agents: **REED, T., David** et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU (utility model), AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, CZ (utility model), DE, DE (utility model), DK, DK (utility model), DM, DZ, EE, EE (utility model), ES, FI, FI (utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KR (utility model), KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

- With international search report.
- Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **ELASTIC ARTICLE**

(57) Abstract: An elastic article is provided which comprises a foam matrix formed from a polymeric material and a plasticiser, a stabilising agent and an active ingredient, such as a detergent active ingredient, typically to be delivered to an aqueous environment. Said elastic article provides a means to deliver an active ingredient to an aqueous environment, preferably the active ingredients being a detergent active ingredient, preferably enzymes, and the aqueous environment being the wash water.

WO 01/25393 A1

ELASTIC ARTICLE

Technical field of the invention

5

The present invention relates to elastic articles, typically particles, comprising a matrix formed from a polymeric material and a plasticiser, a stabilising agent and an active ingredient, such as a detergent active ingredient, typically to be delivered to an aqueous environment.

10

Background to the invention

15

Compositions such as cleaning products and personal care products, cosmetic products and pharmaceutical products, often comprise active ingredients which are to be delivered to water or which are required to be active in an aqueous environment. Many of these active ingredients are sensitive to moisture, temperature changes, light and/or air during storage.

20

Another problem with many of these active ingredients, in particular enzymes, is that they tend to form dust due to physical forces directed upon them during handling. This not only creates waste product, but the dust can also cause hygiene and health problems.

25

Attempts to overcome these problems have led to the development of protecting these active ingredients by coating agents or encapsulating agents. The problem with many of these coated particles is that they do not always exhibit sufficient impact resistance during handling, and when acted upon by physical forces typically encountered during handling, dust is formed which can cause hygiene and health problems.

30

The Inventors have found an improved method of protecting active ingredients and delivering these active ingredients to aqueous environments. They have found that specific elastic articles comprising a foam matrix formed from a polymeric material and a

plasticiser, are very impact robust and the active ingredient which is incorporated therein is protected against physical forces acting upon said elastic article. Furthermore, the Inventors have found that when a stabilising agent is also incorporated in the elastic article, the active ingredient is further protected against air, moisture and chemical
5 reactions which may cause the active ingredient to degrade.

Thus, the elastic article of the present invention is very impact resistant, thus resulting in reduced breaking-up or abrasion during handling and reduced dust formation, and the active ingredient incorporated therein is protected from air, moisture or chemical
10 reactions and remains stable in said article during storage. For example, elastic articles, such as particles or beads, comprising enzymes can be obtained which are safer and more efficient to handle and use. Moreover, these articles can be made such that they deliver the active ingredients incorporated therein, such as enzymes, very efficiently to an aqueous environment. Typically, the article of the present invention is in the form of a
15 foam article which is air-stable under normal humidity storage conditions, but unstable upon contact with water, to thus deliver the active ingredient. The elastic article is useful in any product, especially useful in cleaning products, pharmaceutical products, personal care products, cosmetic products and fabric care products.

20 Summary of the invention

The present invention provides an elastic article comprising;

- a) an active ingredient; and
- b) a foam matrix formed from a polymeric material and a plasticiser; and
- 25 c) a stabilising agent;

whereby said article is capable of delivering said active ingredient to a liquid environment.

The elastic article herein preferably comprises a foam matrix which has a glass transition
30 temperature (T_g) of below 50°C, preferably below 40°C.

The elastic article is preferably in the form of a foam and is stable upon contact with air and unstable upon contact with water, said article preferably having an elastic modulus of less than 0.1 GN.m^{-2} , preferably less than 0.01 GN.m^{-2} .

- 5 The stabilising agent is capable of stabilising the active ingredient of the article herein. The stability of the active ingredient depends on the stability of the foam matrix and or on the stability of the active ingredient itself.

Thus, the stabilising agent may be, or may comprise, a matrix stabilising agent, which is
10 capable of stabilising the foam matrix in the elastic article and during storage of, or the process of preparing, the elastic article.

The active ingredient may also be stabilised by the stabilising agent directly. For example, by increasing the structural stability of the active ingredient. Thus, it may also
15 be preferred that the stabilising agent is, or comprises, an active ingredient stabilising agent

It may also be preferred that the active ingredient of said elastic article comprises at least an enzyme. If an enzyme is comprised by the elastic article herein, then the enzyme may
20 be sensitive to, and denature or start to denature in the presence of, moisture, air or bleach (if present). Therefore, it may be preferred that the stabilising agent is an enzyme stabilising agent, which is capable of stabilising the enzyme in the elastic particle, and during the process of preparing the elastic particle.

- 25 The present invention also relates to processes for making the elastic article. Preferably the elastic article is obtainable by a process comprising the steps of;
- a) obtaining a mixture of a polymeric material and a plasticiser, preferably water and another plasticiser; and
 - b) chemically or physically introducing a gas in said mixture; and
 - 30 c) prior to step b) and/or simultaneous with step b) and /or subsequent to step b), contacting an active ingredient to said mixture; and

- d) prior to step c) and/or simultaneous with step c) and /or subsequent to step c),
contacting a stabilising agent to said mixture; and
e) shaping the articles of the resulting mixture;
whereby preferably one or more steps a) to e) are followed or accompanied by the
5 removal of part of the water, if present.

In another embodiment of the present invention, the use of an elastic article is provided,
to deliver active ingredients to an aqueous environment, preferably the active ingredients
being detergent active ingredients, preferably enzymes, and the aqueous environment
10 being the wash water.

Detailed description of the invention

Elastic article

15

The elastic article of the present invention, herein referred to as “article”, comprises an
active ingredient, a matrix and a stabilising agent. Said active ingredient, matrix and
stabilising agent are described in more detail hereinafter.

- 20 Said article herein is preferably water-dispersible, water-disintegrating or water-soluble.
Preferred water-dispersible articles herein have a dispersibility of at least 50%,
preferably at least 75% or even at least 95%, as measured by the method set out
hereinafter using a glass-filter with a maximum pore size of 50 microns; more preferably
the article herein is water-soluble or water-disintegrating and has a solubility or
25 disintegration of at least 50%, preferably at least 75% or even at least 95%, as measured
by the method set out hereinafter using a glass-filter with a maximum pore size of 20
microns, namely:

- Gravimetric method for determining water-solubility, water-disintegration or water-
30 dispersibility of the article herein:

50 grams \pm 0.1 gram of the article herein is added in a 400 ml beaker, whereof the weight has been determined, and 245ml \pm 1ml of distilled water is added. This is stirred vigorously on magnetic stirrer set at 600 rpm, for 30 minutes. Then, the article-mixture is filtered through a folded qualitative sintered-glass filter with the pore sizes as defined above (max. 20 or 50 microns). The water is dried off from the collected filtrate by any conventional method, and the weight of the remaining article fraction is determined (which is the dissolved, disintegrated or dispersed fraction). Then, the % solubility, disintegration or dispersibility can be calculated.

The article herein is typically used to deliver actives to aqueous environment. Then, the article herein, and preferably the matrix thereof, is preferably unstable when brought into contact with water. This occurs such that the active ingredient(s) or part thereof, present in the article is delivered to a liquid, preferably an aqueous environment such as water. Preferably the article or part thereof denatures, disintegrates, preferably disperses or dissolves in liquid, preferably in an aqueous environment, more preferably in water. It may be preferred that the active ingredient is delivered rapidly to water and that the elastic is such that it disperses or dissolves rapidly; preferably at least 10% of the article, by weight, is dissolved or dispersed in 30 minutes after contacting said article with water, or more preferably at least 30% or even at least 50% or even at least 70% or even at least 90% (introduced in the water at a 1% by weight concentration). It may even be preferred that this happens within 20 minutes or even 10 minutes or even 5 minutes after contacting the article with the water. The dissolution or dispersion can be measured by the method described hereinbefore for measuring the dissolution, disintegration and dispersion of the article herein.

Preferably the elastic article is such that the total volume of the article is changed, preferably reduced, with at least 10%, compared to the initial total volume, as for example can be determined when 1 cm³ of the article is added to 100 ml of demineralised water upon and stirred for 5 minutes at a speed of 200rpm, at a temperature of 25°C.

Preferably the change, or preferably reduction, in total volume is at least 20% or even at least 40% or even at least 60% or even at least 90% or even about 100%, e.g. because it

may be preferred that substantially the whole article is disintegrated, dispersed or preferably dissolved into the water quickly.

This can be measured by use of any method known in the art, in particular herein with a method as follows (double immersion technique):

1 cm³ of an elastic article is obtained and introduced in a 100 ml micro volumetric measuring cylinder which is filled with 50 ml ± 0.1ml of an organic inert solvent. Acetone is for example used when found to be neither denaturing and/or not interacting with the polymeric material in the matrix of the elastic article herein, for example when this is PVA. Other neutral organic medium can be used according to the nature of the article under investigation; the inert solvent is such that the article is substantially not dissolved, dispersed, disintegrated or denatured by the solvent.

The cylinder is air sealed and left to rest for 1 minute so that the solvent penetrates the whole elastic article. The change in volume is measured and taken as the original volume V_i of the foam specimen. The article is then removed from the solvent and left to dry in air so that the solvent evaporates.

The article is then placed in a 250 ml beaker containing 100 ml of demineralised water, maintained at 25°C, under stirring at 200 rpm with the help of a magnetic stirrer, for 5 minutes. The remaining of the article specimen, if any, is filtered off with a 60mm mesh copper filter and placed in an oven at a temperature and for a period such that residual water is removed. The dried remaining article is re-introduced in the measuring cylinder which volume of acetone had been re-adjusted to 50 ml.

The increase in total volume is monitored and taken as the final volume of the elastic article V_f. The decrease in total volume ΔV of the elastic article specimen is then:

$$\% \Delta V = \frac{V_f}{V_i} * 100$$

The elastic article preferably has a relative density ρ* of from 0.01 to 0.95, more preferably from 0.05 to 0.9 or even from 0.1 to 0.8 or even from 0.3 to 0.7. The relative

density is the ratio of the density of the article (ρ^*), to the sum of the partial densities of all the bulk materials used to form article (ρ_s).

5 The preferred foamed article as used herein is typically air-stable or stable upon contact with air, which means herein that the bulk volume of the article or matrix thereof substantially remains the same when exposed to air. This means in particular that the article retains preferably from 75% to 125% or even from 90% to 110% or even from 95% to 100% of its bulk volume when stored in an open beaker (9 cm diameter; without any protective barrier) in a incubator under controlled ambient conditions (humidity = RH
10 60%, temperature = 25°C) for 24 hours. Preferably the elastic article retains from 75% to 125% or even from 90% to 110% or even from 95% to 100% of its bulk volume under the above storage conditions whereby the humidity is 80%.

The bulk volume change can be measured by any conventional method. In particular
15 useful is a digital image recorder system containing a digital camera coupled to a personal computer itself equipped with calibrated image analyser software. A 1cm³ specimen of the article is obtained and introduced in an open beaker having a diameter of 9 cm and stored for 24 hours at the above conditions. After 24 hours, the size in all three dimensions is measured with the image analysis recorder system. Each specimen
20 measurement is repeated three times, and the average bulk volume change is calculated in %.

Preferably, the elastic article is such that, when in the form of particles of a mean particle size of 2000 microns or less, these particles also retain from 75% to 125% or even from
25 90% to 110% or even from 95% to 100% of their bulk volume. This can for example be measured by placing 20 grams of such particles, or a weight comprising more than 500 particles, in a volumetric beaker having a diameter of 9 cm. The beaker is taped lightly on its base until the elastic particles re-arrange themselves in a stable position with a horizontal top surface. The volume is measured. The open beaker with the elastic
30 particles is then carefully placed in the incubator for 24 hours, set to the desired %RH and

temperature. The bulk volume after the 24 hours is measured and the change of bulk volume is calculated in %.

5 The elastic article comprises (by weight) preferably at least 1% active ingredient(s), more preferably from 5% to 70%, more preferably at least 10% by weight of the article, more preferably from 15% or even 20% or even 25% to 50%.

10 The elastic article comprises (by weight) preferably from 10% to 99% matrix, more preferably at least 20% or even 30% to 99%, more preferably from 20% or 30% to 90% to 80%.

15 The elastic article comprises (by weight) at least 1% stabilising agent, more preferably from 5%, or from 10%, or from 15%, or from 20%, and to 50%, or to 40%, or to 30%, or to 25%.

Matrix

20 The matrix of the elastic article of the present invention, herein referred to as "matrix", is formed from a polymeric material and a plasticiser. Said polymeric material and said plasticiser are described in more detail hereinafter.

25 The ratio of plasticiser to polymeric material in the matrix is preferably 1 to 100, more preferably 1 to 70 or 1 to 50, more preferably 1 to 30 or even 1 to 20, depending on the type of plasticiser and polymeric material used. For example, when the polymeric material comprises PVA and the plasticiser comprises glycerine or glycerol derivatives and optionally water, the ratio is preferably around 1:15 to 1:8, a preferred ratio being around 10:1.

30 The matrix herein may further comprise the active ingredient of the article herein and/or the stabilising agent of the article herein. Said active ingredient and said stabilising agent are described in more detail hereinafter. Cross-linking agents may also be added to

modify the properties of the matrix or the resulting article as appropriate. Borate may be useful in the matrix herein.

The matrix herein has a glass transition temperature (T_g) of below 50°C, preferably
5 below 40°C, preferably less than 20°C or even less than 10°C or even less than 0°C.
Preferably the matrix herein has a T_g of above -20°C or even above -10°C.

The T_g of the matrix when used herein, is the T_g of the matrix as present in the article,
which thus may be a mixture of polymeric material and plasticiser alone, or a mixture of
10 polymeric material, plasticiser, active ingredient and/or stabilising agent, and in any case,
optional additional ingredients may be present (such as, densification aids, fillers,
lubricants etc., as described hereinafter).

The T_g as used herein is as defined in the text book 'Dynamic Mechanical Analysis'
15 (page 53, figure 3.11c on page 57), as being the temperature of a material (matrix) where
the material (matrix) changes from glassy to rubbery, namely where chains gain enough
mobility to slide by each other.

The T_g of the matrix of the article of the invention can be measured in the Perkin-Elmer
20 DMA 7e equipment, following the directions in operations manual for this equipment,
generating a curve as illustrated in the book Dynamic Mechanical Analysis - page 57,
figure 3-11c. The T_g is the temperature or log Frequency as measured with this
equipment, between the glass and 'leathery region', as defined in that text.

25 The matrix, and preferably the elastic article as a whole, has a specific elasticity and
flexibility, because of its specific glass transition temperature. In particular, this means
that the matrix and the article reversibly deform, absorbing the energy of impacts or of
forces so that the article or matrix remains substantially its original bulk volume after the
physical force ceases to be applied on the component.

30

The elasticity can be defined by the elastic modulus of the matrix, or even the article, which again can be defined by the Young's modulus. This can be calculated from strain or stress mechanical tests as known in the art, for example by using Perkin-Elmer DMA 7e equipment following the manufacturer's experimental procedure over a specific % static strain range, namely in the range of 10-40% static strain. This represents a maximum strain as could be applicable during normal manufacturing or handling. Thus, the elastic modulus as defined herein is the maximum modulus as measured with this equipment in the range of 10% to 40% static strain. For example a piece of matrix (or article) of 1 cm³ can be used in the testing with this equipment.

The matrix herein typically has an elastic modulus or Young's modulus of less than 4 GN.m⁻², or typically less than 2 GN.m⁻², even more preferentially less than 1 GN.m⁻², but typically even less than 0.5 GN.m⁻², or even less than 0.1 GN.m⁻², or even less than 0.01 GN.m⁻², as measured with the Perkin-Elmer DMA 7e equipment. In particular a matrix herein which contains gas bubbles, e.g. formed by processes involving the introduction of air in the matrix, has an elastic modulus below 0.1 GN.m⁻² or even 0.01 GN.m⁻² or even below 0.005 GN.m⁻² or even below 0.0001 GN.m⁻².

Preferably the matrix is flexible, such that it has a relative yield strain greater than 2%, and preferably greater than 15% or even greater than 50%, as measured with the Perkin-Elmer DMA 7e equipment. (The yield strain is, in this measurement, the limit of strain at which a piece of matrix deforms irreversible).

In particular this means that when a matrix sample having a cross section of a specific length, for example 1cm, is compressed with a static force applied along the axis of that cross section, the static force being variable but at least equivalent to twice atmospheric pressure, the change of this length after removal of the force is at least 90% to 110% of the original length. This can for example be measured by use of Perkin-Elmer DMA 7e equipment.

Similarly, the matrix is preferably flexible to such an extent that when a matrix sample having a cross section of a specific length, for example 1cm, is stretched with a static force applied along the axis of that cross section, the static force being variable, but at least equivalent to twice atmospheric pressure, the change of this length after removal of the force is at least 90% to 110% of the original length. This can for example be measured by use of Perkin-Elmer DMA 7e equipment.

In particular, when using this equipment, the static forces applied along the axis of a cross section of a 1 cm³ matrix sample are gradually increased until the deformation of the component, in the direction of the cross section, is 70%. Then, the force is removed and the final deformation of the matrix sample in the direction of the cross section is measured. Preferably, this length of the cross section after this experiment is preferably from 90% to 110% of the original length of the cross section, preferably from 95% to 105% or even from 98% to 100%.

The elastic modulus or Young's modulus is related to the relative density, namely

$$\frac{E^*}{E_s} \approx \left(\frac{\rho^*}{\rho_s} \right)^2,$$

where ρ^* is the relative density of the matrix or even the article, and ρ_s is the relative densities of the components of the matrix or article, as described herein, and E^* is the Young's modulus of the matrix or even the elastic article itself, and E_s that of the components of the matrix or even the article. This means that even a stiff polymeric material, with a high E_s can be made into an elastic, flexible matrix by adjusting the levels and/ or type of plasticiser and optionally by modifying the density (or for example by introducing gas during the making process to form elastic foam articles, as described below).

The matrix, or even the article as a whole, is preferably in the form of a foam and preferably such that it forms an interconnected network of open and/ or closed cells, in particular a network of solid struts or plates which form the edges and faces of open and/

or closed cells. The spacing inside the cells can contain part of the active ingredient and/or a gas, such as air.

Preferably, the ratio of the closed cells to open cells in the matrix of the article, or the article as a whole is more than 1:1, preferably more than 3:2 or even more than 2:1 or even more than 3:1. This ratio can be determined by calculating the Total Volume of a specimen of the matrix or article, V_T , (assuming a spherical shape), and then measuring with a Mercury Porosimetry Test method the Open Cell Volume (V_O) and subtracting the Open Cell Volume from the Total Volume should deliver the Closed Cell Volume (V_C :
10 $V_T = V_O + V_C$).

Polymeric material

Any polymeric material can be used to form the matrix herein, provided it has itself a T_g as defined above or more typically, it can be formed into a matrix having the T_g as defined above by using a suitable amount of plasticiser.
15

Preferably, the polymer material comprises or consists of amorphous polymer(s).

20 The polymeric material may consist of a single type of homologous polymer or may be a mixture of polymers. Mixtures of polymers may in particular be beneficial to control the mechanical and/or dissolution properties of the elastic article, depending on the application thereof and the requirements thereof.

25 Preferred it that the polymeric material comprises a water-dispersible or more preferably a water-soluble polymer. Water-dispersible and water-soluble are typically defined as described hereinbefore, as per the method for determining the water-solubility and water-dispersibility of the article herein. Preferred water-dispersible polymers herein have a dispersibility of at least 50%, preferably at least 75% or even at least 95%, as measured
30 by the method set out hereinbefore using a glass-filter with a maximum pore size of 50 microns; more preferably the polymer herein is a water-soluble polymer which has a

solubility of at least 50%, preferably at least 75% or even at least 95%, as measured by the method set out hereinbefore using a glass-filter with a maximum pore size of 20 microns.

- 5 The polymer can have any average molecular weight, preferably from about 1000 to 1,000,000, or even from 4000 to 250,000 or even from 10,000 to 200,000 or even from 20,000 to 75,000. Highly preferred may be polymeric material having a weight average molecular weight of from 30,000 to 70,000.
- 10 Depending on the required properties of the article herein, the polymeric material can be adjusted. For example, to reduce the solubility, polymers may be included in the material, which have high molecular weights typically above 50,000 or even above 100,000, and vice versa. For example, to change the solubility, polymers of varying level of hydrolyses may be used. For example, to improve (reduce) the elastic modulus, the
- 15 cross-linking of the polymers may be increased and/ or the molecular weight may be increased.

It may be preferred that the polymer used in the elastic article herein has a secondary function, for example a function in the composition wherein article is to be incorporated.

- 20 Thus for example for cleaning products, it is useful when the polymer in the polymeric material is a dye transfer inhibiting polymer, dispersant etc.

Preferred are polymers selected from polyvinyl alcohols and derivatives thereof, polyethylene glycols and derivatives thereof, polyvinyl pyrrolidone and derivatives

25 thereof, cellulose ethers and derivatives thereof, and copolymers of these polymers with one another or with other monomers or oligomers. Most preferred are PVP (and derivatives thereof) and/ or PEG (and derivatives thereof) and most preferably PVA (and derivatives thereof) or mixtures of PVA with PEG and/ or PVP (or derivatives thereof). Most preferred may also be a polymeric material only comprising PVA.

- 30 Preferably, such polymers have a level of hydrolysis of at least 50%, more preferably at least 70% or even from 85% to 95%.

Plasticiser

Any plasticiser which is suitable to aid the formation of a matrix as defined herein can be
5 used. Mixtures of plasticiser may also be used. Preferably, when water is used, an
additional plasticiser is present.

Preferably, the plasticiser or at least one of the plasticisers, has a boiling point above
40°C, preferably above 60°C, or even above 95°C, or even above 120°C, or even above
10 150°C.

Preferred plasticisers include glycerol or glycerine, glycol derivatives including ethylene
glycol, digomeric polyethylene glycols such as diethylene glycol, triethylene glycol and
tetraethylene glycol, polyethylene glycol with a weight average M.W. of below 1000,
15 wax and carbowax, ethanolacetamide, ethanolformamide, triethanolamine or acetate
thereof, and ethanolamine salts, sodium thiocyanates, ammonium thiocyanates, polyols
such as 1,3-butanediol, sugars, sugar alcohols, ureas, dibutyl or dimethyl phthalate, oxa
monoacids, oxa diacids, diglycolic acids and other linear carboxylic acids with at least
one ether group distributed along the chain thereof, water or mixtures thereof.

20 The plasticiser is preferably present at a level of at least 0.5% by weight of the article,
preferably by weight of the matrix, provided that when water is the only plasticiser it is
present at a level of at least 3% by weight of the article, or preferably by weight of the
matrix.

25 Preferably, the plasticiser is present at a level of 1% to 35% by weight of the article or
matrix, more preferably 2% to 25% or even to 15% or even to 10% or even to 8% by
weight of the article or by weight of the matrix. The exact level will depend on the
polymeric material and plasticiser used, but should be such that the matrix of the article
30 has the desired Tg. For example, when urea is used, the level is preferably 1% to 10% by
weight of the matrix, while when glycerine or ethylene glycol or other glycol derivatives

are used, higher levels may be preferred, for example 2% to 15% by weight of the article or matrix.

Active ingredient

5

The active ingredient can be any material which is to be delivered to a liquid environment, or preferably an aqueous environment and preferably an ingredient which is active in an aqueous environment. For example, when used in cleaning compositions the article can contain any active cleaning ingredients. The articles may also comprise compositions, such as cleaning composition or personal care compositions.

10

In particular, it is beneficial to incorporate in the elastic article active ingredients which are moisture sensitive or react upon contact with moisture, or solid ingredients which have a limited impact robustness and tend to form dust during handling.

15

The active ingredient is typically a moisture sensitive ingredient, a temperature sensitive ingredient, an oxidizable ingredient, a volatile ingredient, or a combination thereof. The active ingredient may be biological viable material, hazardous or toxic material an agricultural ingredient such as an agrochemical, a pharmaceutical ingredient such as a medicine or drug, or a cleaning ingredient.

20

In particular preferred in elastic articles are active ingredients, such as enzymes, perfumes, bleaches, bleach activators, fabric cationic and/or silicone softeners and/or conditioners, antibacterial agents, effervescence sources, brighteners, photo-bleaches and mixtures thereof.

25

A preferred active ingredient is a perhydrate bleach, such as metal perborates, metal percarbonates, particularly the sodium salts. Also preferred active ingredients are organic peroxyacid bleach precursor or activator compound, preferred are alkyl percarboxylic precursor compounds of the imide type include the N-,N,N¹N¹ tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly

30

those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms such as tetraacetyl ethylene diamine (TAED), sodium 3,5,5-tri-methyl hexanoyloxybenzene sulfonate (iso-NOBS), sodium nonanoyloxybenzene sulfonate (NOBS), sodium acetoxybenzene sulfonate (ABS) and pentaacetyl glucose, but also amide substituted
5 alkyl peroxyacid precursor compounds

Highly preferred active ingredient for use in the elastic article herein are one or more enzymes. Preferred enzymes include the commercially available lipases, cutinases, amylases, neutral and alkaline proteases, cellulases, endolases, esterases, pectinases,
10 lactases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139. Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Industries A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades,
15 those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Preferred amylases include, for example, α -amylases obtained from a special strain of *B licheniformis*, described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold under the tradename
20 Termamyl, Duramyl and BAN by Novo Industries A/S. Highly preferred amylase enzymes maybe those described in PCT/ US 9703635, and in WO95/26397 and WO96/23873. The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of *Humicola* sp., *Thermomyces* sp. or *Pseudomonas* sp. including *Pseudomonas pseudoalcaligenes* or *Pseudomas fluorescens*.
25 Lipase from chemically or genetically modified mutants of these strains are also useful herein. A preferred lipase is derived from *Pseudomonas pseudoalcaligenes*, which is described in Granted European Patent, EP-B-0218272.

Another preferred lipase herein is obtained by cloning the gene from *Humicola lanuginosa* and expressing the gene in *Aspergillus oryza*, as host, as described in

30 European Patent Application, EP-A-0258 068, which is commercially available from

Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Høge-Jensen et al, issued March 7, 1989.

Stabilising agent

5

The article herein comprises a stabilising agent, which is typically capable of stabilising the active ingredient of the article herein, this is especially preferred when the active ingredient(s) comprise an oxidative or moisture sensitive active ingredient, such as one or more enzymes. The stabilising agent may also stabilise the matrix of the article herein, and thus indirectly stabilise the active ingredient.

10

The stabilising agent is preferably a compound which stabilises the active ingredient, or matrix, from oxidative and/or moisture degradation during storage.

15

The stabilising agent is in addition to the active ingredient of the article herein. If more than one active ingredient is comprised by the article herein, then it may be preferred that one of the active ingredients is selected such that is, or acts as, a stabilising agent. For the purpose of the present invention, the stabilising agent is always an additional component of the article herein to the active ingredient of the article herein.

20

Therefore, for the purpose of the present invention, for an article to be defined as comprising a stabilising agent and an active ingredient, wherein said article comprises a component having dual functionality and can function as an active ingredient or a stabilising agent as defined herein, an additional stabilising agent or active ingredient must be present in the article herein, which is in addition to the compound having dual functionality, to obtain an article comprising an active ingredient and a stabilising aid which is in accord with the present invention.

25

The above statements with regard to ingredients having dual functionality are also true when considering other embodiments of the present invention. It is essential for the article herein to comprise an active ingredient, a polymeric material and a plasticiser

30

(which form the matrix), and a stabilising aid. Thus, to obtain an article in accord with the present invention, at least four different ingredients must be present in said article. It may be preferred to select essential ingredients which have dual functionality.

- 5 The above statements with regard to dual functionality ingredients are also true when considering highly preferred embodiments of the present invention, for example preferred articles comprising additional ingredients such as a dissolution aid.

The stabilising agent may be, or comprise, a foam matrix stabiliser. The stabilising agent
10 may be, or comprise, an active ingredient stabiliser, especially an enzyme stabiliser.

Stabilising agents which are capable of stabilising the active ingredient indirectly by keeping the foam matrix of the article stable, herein referred to as "foam stabiliser" preferably comprise a surfactant such as a fatty alcohol, fatty acid, alkanolamide, amine
15 oxide, or derivatives thereof, or combinations thereof. The foam stabiliser may comprise betaine, sulfobetaine, phosphine oxide, alkyl sulfoxide, derivatives thereof, or combinations thereof.

Other preferred foam stabilisers comprises one or more anions or cations such as mono-,
20 di-, tri- valent, or other multivalent metal ions, preferred are salts of sodium, calcium, magnesium, potassium, aluminium, zinc, copper, nickel, cobalt, iron, manganese and silver, preferably having an anionic counterion which is a sulphate, carbonate, oxide, chloride, bromide, iodide, phosphate, borate, acetate, citrate, and nitrate, and combinations thereof.

25

The foam stabiliser may comprise finely divided particles, preferably finely divided particles having an average particle size of less than 10 micrometers, more preferably less than 1 micrometer, even more preferably less than 0.5 micrometers, or less than 0.1 micrometers. Preferred finely divided particles are aluminosilicates such as zeolite, silica,
30 or electrolytes described hereinbefore being in the form of finely divided particles.

The foam stabiliser may comprise agar-agar, sodium alginate, sodium dodecyl sulfate, polyethylene oxide, guar gum, polyacrylate, or derivatives thereof, or combinations thereof.

- 5 The foam stabiliser may be coating which is separate to the matrix of the article herein. The foam stabiliser typically partially encloses, preferably completely encloses, the article herein or the active ingredient thereof.

10 The coating is typically contacted to, preferable in such a manner as to form a coat on, the active ingredient prior to said active ingredient being contacted to the polymeric material or the plasticiser of the matrix, and preferably being incorporated in the article herein.

15 The coating may typically be contacted to, preferable in such a manner as to form a coat on, the article herein subsequent to the polymeric material and the plasticiser forming the matrix, and preferably subsequent to the active ingredient contacting said matrix or being incorporated in the article herein.

20 Preferred coating comprises polymers, typically selected from polyvinyl alcohols and derivatives thereof, polyethylene glycols and derivatives thereof, polyvinyl pyrrolidone and derivatives thereof, cellulose ethers and derivatives thereof, and copolymers of these polymers with one another or with other monomers or oligomers. Most preferred are PVP (and derivatives thereof) and/ or PEG (and derivatives thereof) and most preferably PVA (and derivatives thereof) or mixtures of PVA with PEG and/ or PVP (or derivatives thereof). These polymers do not form the matrix of the article herein. Thus, these
25 polymers are different to the polymeric materials of the foam matrix.

30 A preferred coating comprises compounds such as glycerol or glycerine, glycol derivatives including ethylene glycol, digomeric polyethylene glycols such as diethylene glycol, triethylene glycol and tetraethylene glycol, polyethylene glycol with a weight average M.W. of below 1000, wax and carbowax, ethanolacetamide, ethanolformamide, triethanolamine or acetate thereof, and ethanolamine salts, sodium thiocyanates,

ammonium thiocyanates, polyols such as 1,3-butanediol, sugars, sugar alcohols, ureas, dibutyl or dimethyl phthalate, oxa monoacids, oxa diacids, diglycolic acids and other linear carboxylic acids with at least one ether group distributed along the chain thereof, water or mixtures thereof. These compounds do not form the foam matrix of the article herein.

5 Thus, these compounds are different to the plastisicer of the foam matrix.

Preferred stabilising agents that are capable of stabilising the active ingredient directly, especially if said active ingredient comprises one or more enzymes, are defined herein as “active stabilisers” or “enzyme stabilisers”. Typically active stabilisers interact directly
10 with, and stabilise, the active ingredient.

Typical active stabilisers for use herein preferably comprise a surfactant. Suitable surfactants for use herein are those described hereinbefore as surfactants suitable for use as matrix stabilisers. In addition to these surfactants, other surfactants suitable for use
15 herein may comprise surfactants such as sodium alky(en)yl sulfonates, sodium alkoxysulfonates, preferred alkoxysulfonates are those comprising from 10 to 18 carbon atoms in any conformation, preferably linear, and having an average ethoxylation degree of from 1 to 7, preferably from 2 to 5.

20 Other preferred active stabilisers comprise boric acid, formic acid, acetic acid, and salts thereof. These acid salts preferably comprise counerions such as calcium and/or sodium.

Preferred active stabilisers comprise cations such as calcium and or sodium. Preferably calcium chloride and/or sodium chloride.

25 Other preferred active stabilisers comprise small peptide chains averaging from 3 to 20, preferably from 3 to 10 amino acids, which interact with and stabilise the active ingredient, especially enzyme(s).

30 Other active stabilisers comprise small nucleic acid molecules, typically comprising from 3 to 300, preferably from 10 to 100 nucleotides. Typically nucleic acid molecules are

deoxyribonucleic acid and ribonucleic acid. The nucleic acid molecules may be in the form of a complex with other molecules such as proteins, or may form a complex with the active ingredient of the article herein, especially enzyme(s).

- 5 Active stabilisers suitable for use herein, especially when the article herein comprises a bleach, comprise anti-oxidants and/or reducing agents such as thiosulphate, methionine, urea, thiourea dioxide, guanidine hydrochloride, guanidine carbonate, guanidine sulfamate, monoethanolamine, diethanolamine, triethanolamine, amino acids such as glycine, sodium glutamate, proteins such as bovine serum albumin and casein, tert-
- 10 butylhydroxytoluene, 4,4,-butylidenebis (6-tert-butyl-3-methyl-phenol), 2,2'-butlidenebis (6-tert-butyl-4-methylphenol), (monostyrenated cresol, distyrenated cresol, monostyrenated phenol, distyrenated phenol, 1,1-bis (4-hydroxy-phenyl) cyclohexane, or derivatives thereof, or a combination thereof.
- 15 Other active stabilisers may comprise a reversible inhibitor of the active ingredient. Without wishing to be bound by theory, it is believe that a reversible inhibitor of the active ingredient, especially if the active ingredient comprises one or more enzymes, may form a complex with, and improve the stability of, said active ingredient, and thus, stabilises the active ingredient during storage. When the active ingredient is released,
- 20 typically into a liquid environment, the reversible inhibitor dissociates from the active ingredient and the active ingredient is then able to perform the desired action it is designed or intended to perform.

- Active stabilisers suitable for use herein may comprise sugars, Typical sugars for use
- 25 herein include those selected from the group consisting of sucrose, glucose, fructose, raffinose, trehalose, lactose, maltose, derivatives thereof, and combinations thereof.

The active stabiliser may also comprise sugar alcohols such as sorbitol, mannitol, inositol, derivatives thereof, and combinations thereof.

30

It may be preferred that the active stabiliser is in the form of a coating or barrier which at least partially encloses the article herein or the active ingredient thereof, preferably completely encloses the article herein or the active ingredient thereof, especially an enzyme.

5

The article herein may comprise (by weight) from 0.01%, or from 0.1%, or from 1%, or from 2%, or from 5%, or from 7%, or from 10%, or from 15%, or from 20% stabilising agent, and may comprise (by weight) to 70%, or to 60%, or to 50%, or to 40%, or to 30%, or to 25% stabilising agent. The amount of stabilising agent present in the article depends on the amount and type of the active ingredient and on the amount and type of the matrix herein.

10

Additional Ingredients

15 The component of the invention preferably comprises additional ingredients which can improve the dissolution properties of the article herein.

Preferred additional ingredient which improve the dissolution of the article herein preferably comprise; a sulfonated compound such as C₁-C₄ alk(en)yl sulfonates, C₁-C₄ aryl sulfonates, di iso butyl benzene sulphonate, toluene sulfonate, cumene sulfonate, xylene sulfonate, salts thereof such as sodium salts thereof, derivatives thereof, or combinations thereof, preferably di iso butyl benzene sulphonate, sodium toluene sulfonate, sodium cumene sulfonate, sodium xylene sulfonate, and combinations thereof; and/or a C₁-C₄ alcohol such as methanol, ethanol, propanol such as iso-propanol, and derivatives thereof, and combinations thereof, preferably ethanol and/or iso-propanol; and/or a C₄-C₁₀ diol such as hexanediol and/or cyclohexanediol, preferably 1,6-hexanediol and/or 1,4-cyclohexanedimethanol; and/or ingredients which are capable of acting as whicking agents, such as cellulosic based ingredients, especially modified cellulose; and/or swelling agents such as clays, preferred clays are smectite clays, especially dioctahedral or trioctahedral smectite clays, highly preferred clays are montmorillonite clay and hectorite clay, or other clays found in bentonite clay

20

25

30

formations; and/or an effervescence system, a preferred effervescence system comprises an acid source capable of reacting with an alkali source in the presence of water to produce a gas.

5 Process for making elastic article

The elastic article of the invention can be made by any process of making a polymer matrix of the defined Tg from a polymeric material and a plasticiser, and combining an active ingredient and a stabilising agent with such a matrix. Preferred processes involve
10 chemically or physically introducing a gas in a mixture of the polymeric material and plasticiser and optionally the active ingredient.

A preferred process for making the article herein comprising the step of

- 15 a) obtaining a mixture of a polymeric material and a plasticiser, preferably water and an additional plasticiser;
 - b) chemically or physically introducing gas in said mixture of polymeric material and water;
 - c) prior to step b) and/or simultaneously with step b) and/ or subsequently to step b), addition of the active ingredient to said mixture;
 - 20 d) prior to step c) and/or simultaneously with step c) and/ or subsequently to step c), contacting a stabilising agent to said mixture;
 - e) shaping the articles of the resulting mixture;
- whereby one or more of steps a) to e) are followed or accompanied by removal of part of the water, if present.

25

In step a) the mixture is preferably an aqueous mixture or slurry and after or in step b), c) and/ or d), part of the water is removed such that the resulting article comprises 3% by weight of free-moisture, or more.

30 Step c) preferably comprises the step of obtaining a body comprising the active ingredient or part thereof and enclosing said body with the mixture of step b).

Step d) preferably comprises the step of mixing, more preferably intimately mixing or enclosing, the active ingredient with the stabilising agent.

5 Preferably, the article comprises open and/ or closed cells and the process comprising the steps of

a) formation of a mixture of the polymeric material, the active material, a stabilising agent, a plasticiser and a liquid, whereby the liquid and the plasticiser may be the same compound;

10 b) shaping of bodies from the mixture of claim b) and

c) evaporation of the liquid or part thereof to form spacings in the mixture which form the inner area of the cells of the article, whereby step c) is preferably conducted by freeze drying or by heating the bodies, thereby causing the liquid or part thereof to evaporate.

15

Step b) may also be conducted by submitting the mixture of a) to pressure, preferably under mixing and/ or increasing the temperature, and subsequently removing the pressure or part thereof, thereby causing the liquid to evaporate. For example, an extrusion process can be used. Hereby it is preferred that the mixture of the polymeric material, plasticiser, preferably including water, and optionally the active ingredient, is introduced in an extruder, wherein the mixture is further mixed and heated, due to the mixing or due to applying heat, preferably such that the mixture therein forms a melt, and then dropping the pressure at the exit point where the extruded mixture (which can be formed into the desired form, for example granules) exits the extruder, whereby the liquid or part thereof evaporates, or preferably the water evaporates as steam from the extruded mixture. This results in formation of cells with spacings, as described above, which then may contain a gas, preferably air, and optionally the active ingredient. These spacings form the internal area of the cells of the matrix of the elastic article of the invention.

20
25
30 Step b) in the process may also be conducted by heating the mixture to cause the liquid or part thereof to evaporate, resulting in the formation of spacings, as above. This can

preferably done by feeding the mixture into a spray drying tower, preferably such that the mixture is fed through spray nozzles which form droplets of the mixture, and spray drying the droplets at conventional, resulting in granules of the elastic article.

5 The physical and/ or chemical introduction of gas or foaming, as mentioned above can be done by any known method, preferred are

- physical foaming by gas injection (dry or aqueous route) optionally under mixing, high shear stirring (dry or aqueous route), gas dissolution and relaxation including critical gas diffusion (dry or aqueous route);
- 10 - chemical foaming by in-situ gas formation (via chemical reaction of one or more ingredients, including formation of CO₂ by an effervescence system),
- steam blowing, UV light radiation curing.

These foaming steps are preferably followed by a drying step or an additional drying step
15 to remove excess liquid or part thereof, such as water. In particular, the drying step is at least done after the polymer matrix is formed, and optionally after the active ingredient is added, preferably as final step in the process. The drying step is done preferably such that the final elastic article is of about the same volume after the drying step as before the drying step. Thereto, the drying step is preferably done by freeze-drying, whereby the
20 solvent, e.g. water, is removed under vacuum and reduced temperatures. Also useful can be slow fluid bed drying or oven drying at modestly increased temperatures, such as 40-80°C, or even 40-60°C .

Preferred processes involve at least the step of formation of a mixture of polymeric
25 material and a liquid, preferably a solution of polymeric material and a solvent, preferably comprising water, and adding a plasticiser (or as the case may be, additional plasticiser) to this. If the presence of the active ingredient and/or the stabilising agent in the matrix is required, these are also added to the mixture of polymeric material solvent and plasticiser. Alternatively, or in addition, it may be preferred that the matrix is formed around the
30 active material, preferably a core of the active material and carrier material.

This is then further processed for example into bodies of the shape of the final article, for example particles or beads, and typically dried to obtain the articles. Preferably, a gas is added prior to the shaping step. Shaping steps include granulation steps such as atomisation or spray-drying, extrusion, micro pastillisation. Freeze drying is a preferred process to dry the bodies to form the articles.

The following are preferred processes resulting in low dust or even nil dust particles, as measured with the stressed Heubach test described below, having a matrix with a Tg of below 10°C and an elastic modulus of below 0.5GNm⁻², as indicated in more detail in the following specific examples.

A first preferred process is as follows:

The required amount of a solution of the polymer material (or a mixture of polymer and a liquid) is obtained, and for example (introduced) in a mix tank. Then the required amount of (a solution of) the active material, for example an enzyme solution, and stabilizing agent is added, and the required amount of plasticiser is added, and optionally other additional ingredients, such as fillers, densification agents etc. This is agitated to become a homogeneous mixture. Preferably, a gas such as air can be introduced into the solution, by any of the methods above, preferably physically, by high sheer mixing.

Then, particles are formed from this mixture by atomisation, preferably using a Positive Displacement pump to transfer the mixture solution to a spray nozzle (s), preferably using either single or multi-fluid nozzles to create liquid droplets.

The liquid droplets are then frozen, preferably by passing through a refrigeration media (can include liquid nitrogen, freon, refrigeration oils). Then, the frozen particles are transferred to a vacuum chamber, preferably having a temperature (as measured on the surface of the particles) below 0°C.

The frozen particles are preferably collected from the spray column and transferred without raising the temperature. The temperature of the walls and contact trays of the freeze dryer are preferably maintained below 0°C to keep the particles frozen.

A vacuum is applied, and the frozen ice crystals will sublimate said gas to a gaseous

form, resulting in cells in the particle. The total drying degree can be controlled with the level of vacuum, and contact temperature of the chamber walls and trays.

After the particles have been dried to the desired moisture content, they will be free flowing. Then preferably, the particles can be classified via a variety of screens and or process equipment.

The optional step above, of introducing gas (bubbles) into the polymeric solution mixture has been found to give a much better impact resistance to the particle, reflected by its electric modules. The introduction of gas bubbles can be accomplished in a variety of ways.

In the atomisation step, the atomizing nozzle should preferably be located in a spray column with sufficient height to accomplish droplet freezing while gravity falling. The nozzle type can be of various designs - single fluid pressure nozzle, spinning insert, sonic, or multi-fluid nozzle. The important aspect is to disrupt the liquid stream to form discrete liquid droplets. As these droplets fall with gravity, they need to be cooled to freezing. The freezing media is preferably non-aqueous gas or liquid which can provide rapid freezing of the liquid droplets. The actual temperatures for cooling these droplets to form particles, is preferably below 0°C and preferably below -20°C.

It may also be preferred that the above process is modified as follows:

a gas, preferably CO₂ gas, is introduced in the mixture and the mixture is introduced in a spray drying tower, as above, thereby forming spray-dried foamed particles, which can be classified if necessary. Preferably the inlet temperature in the tower is about 130°C and the outlet temperature about 75°C and the spray rate is 12.5g/min. For example a Niro Mobil Minor with two fluid nozzles can be used hereby. The resulting particle may be already of the required form, or may be submitted to further freeze drying under vacuum.

Another preferred process is as follows:

The required amount of a solution of the polymer material is obtained (or alternatively, a powdered polymer can be used provided a liquid is added) and for example introduced in

a mix tank. Then the required amount of plasticiser is added, and optionally other additional ingredients, such as fillers, densification agents etc. This is agitated to become a homogeneous mixture. Preferably, a gas such as air can be introduced into the solution, by any of the methods above, preferably physically, by high sheer mixing.

5

Also, particles comprising the active ingredient, such as an enzyme, and the stabilising agent, and optionally other ingredients, such as fillers or carriers are prepared, for example by fluid bed coating, by charging first 'cores' (typically when the actives care enzymes, these core particles are sugar or starch particles), to a fluid bed and spraying the active material or a solution of the active material onto these cores and then drying any solvent such as water from the active solution off with warm fluidizing air.

10

Then, the polymeric mixture above is introduced onto these active/cores , for example via a positive displacement pump leading to an atomizing nozzle inside the fluid bed as described above. More than one nozzle can be used and it may be preferred that different ingredients are added to the core via different nozzles.

15

The fluidizing air needs is preferably below 0°C, preferably around -20°C. Then, the fluidizing air freezes the polymeric mixture/solution onto the outside of the active-core. This is a critical parameter to control and typically the air temperature must be below 0°C in order to quickly freeze the polymeric mixture/solution onto the core particles.

5

Then preferably, the frozen particles thus obtained are transferred to a vacuum chamber, as above, and also classification may take place.

10 This technology results in particle of the invention comprising a matrix around the active ingredient.

The optional step above, of introducing gas (bubbles) into the polymeric solution mixture has been found to give a much better impact resistance to the particle, reflected by its Young's Modulus.

15 Another preferred process is as follows:

The required amount of a solution of the polymer material (or solid polymer and a suitable amount of liquid) is obtained, and for example introduced in a mix tank. Then the required amount of (a solution of) the active material, for example an enzyme
20 solution, and a stabilising agent (a solution of) is added (into the mix tank) and the required amount of plasticiser is added, and optionally other additional ingredients, such as fillers, densification agents. This is agitated to become a homogeneous mixture. Preferably, a gas such as air can be introduced into the solution, by any of the methods above, preferably physically, by high sheer mixing.

25

Then, the polymeric solution is pumped from the mix tank into an extruder or into a cavity with a die plate at the end. Before entering the extruder or cavity, gas can be injected into the mixture and for example be dispersed via a mechanical shear mixer or a static mixer.

30 As the extrudate exits the die plate, the change in pressure creates a slight puffing or swelling in the extrudate. The extrudate is then cut to the correct length with either a die face cutter or with some other device (e.g. heated wire, rotating plug cutter, etc.). The

extrudates can optionally go through additional rounding steps to become more spherical. Process equipment that can accomplish this function include (rotating pans, agglomeration pans, marumerizers, tumbling drums, mixing drums, etc.).

- 5 For example, a paste is prepared by mixing 75g PVOH, 15g Citric acid, 2g PEO and 22.5g glycerol in a Braun mixer, high sheer, namely set at full speed for 40seconds: then 80g H₂O and 80g enzyme was added and mixed at high sheer, namely set at full speed until a smooth foam had formed, approximately within 2mins. The foam was extruded from a 10ml syringe onto a plastic sheet. This was left for 24 hours to dry. Once dry the
- 10 foam strips were cut into approximately 1 - 2mm sections to form particles of the formula (dry) 63.2 polyvinyl alcohol, 19% glycerol, 12.7% citric acid, 1.6% PEO, 4% water, 3.2% enzyme.

The resulting particles had an elastic modulus of 0.00016GN.m⁻².

15

The resulting particles give 0% dusting when tested in a stressed Heubach test, which indicated a very good impact robustness. (The stressed Heubach test is performed as known in the art, using equipment as supplied by Heubach Engineering GmbH, Germany, with the stressed modification of the rotation speed of the impeller being 75 ±

20 1 rpm and the balls being of Tungsten carbide and 82 grams each.).

Preferred moulding / pastillisation process:

A highly preferred process involves shaping particles of mixtures as described above by use of a mould; whereby mixtures as described herein are introduced in a mould and subsequently dried (freeze dried). Also preferred is such a process which uses pastille making equipment, whereby mixtures as described above, preferably comprising also
5 introduced gas, are forced through a rotating perforated drum onto a moving conveyor belt, shaping into pastilles (droplets or particles). When dry or hardened, the thus formed particles or beads are removed from the conveyor belt by a scraper.

Preferably, the first step is to make a mixture of polymeric material and plasticiser, a
10 liquid component, and optionally the active ingredient. Preferably, gas is introduced into this mixture as described herein. This must preferably be free from large undissolved particles which may block up the perforations in the drum. The mixture is preferably in the temperature range 0-50°C. The mixture is pumped into a manifold that enters the rotating perforated drum and is parallel to the longitudinal axis of the drum. The mixture
15 is pumped into the inner of the drum and, as the drum rotates, is brought into contact with an internal scraper bladed lying in contact and along the length of the inner surface of the perforated drum, parallel to the feed manifold.

The distance of the outside surface of the perforated drum is within the height of the
20 desired particle height (which is less than the diameter of the perforations) but not touching a moving conveyor belt or a rotating smooth surfaced drum at the point where the internal scraper is in contact with the inner surface of the perforated drum, the tangential speed of the perforated drum matched by the speed of the conveyor belt or the tangential speed of the smooth surfaced drum. As the mixture is forced through the
25 perforations, which are typically in the size range 300 - 2000µm (but may be smaller or larger), it is deposited onto the surface below. The rotation of the perforated drum shears the feed material away from the material on the smooth surface thus leaving a droplet, or pastille, which will form the required particle. These pastilles can be set by either chilling or by evaporation of some or all of the solvent fluid. If chilling is required the
30 temperature of the conveyor belt or smooth surfaced drum may be in the range of from ambient to -20°C. If evaporation of a solvent is required, then this can be achieved by heat conduction from the conveyor belt which may be in the range ambient to 70°C, by

drying air (which may be heated up to 200°C to reduce drying time) passing over the surface of the pastilles, or both.

Then, the resulting particles are removed from the drum or conveyor belt by a scraper.

This removal process may be improved by the use of a suitable lubricant (release agent)

5 on the drum, such as silicone oil. This lubricant or release agent may show an added benefit to the particle by reducing adhesive properties between the polymeric mixture and the belt/drum and thus increasing the pastille height, if this is a desirable feature.

Examples

10

Example 1

-

A process of preparing an elastic article in accord with the present invention

15

4700g of a 33%w/w solution of polyvinyl alcohol (weight average M.W being from 30,000 to 70,000) is mixed with 3360g enzyme solution (5% by weight active enzyme and 85% by weight water), 159.3g of glycerol and 168g of ammonium sulphate in a high shear mixer until a smooth foam is formed. This mixture is transferred into a feed tank, and using a gear pump, it is pumped into micropastillisation equipment, for example as supplied by Sandvik Process Systems, Totowa New York, using a perforated drum with perforations of 1mm diameter, spaced 2.5mm apart. The apparatus deposits pastilles onto a smooth surfaced drum coated with a film of silicone oil and heated to ~30°C. When one quarter of the drum is covered by pastilles, the drum is stopped from rotating. The pastilles are dried using a hot air heater until the surfaces of the pastilles are dry to the touch. The resulting particles are then scraped off and collected.

25

Example 2

30

A process of making foamed articles of the invention, in the form of tablets, beads or particles

Apparatus: Microbalance, graduated 100ml flask, Kenwood "Chef" food processor with provided whisk and mixing bowl, glass or plastic moulds, spatula.

Chemicals: Poly (vinyl alcohol) (Aldrich chemicals, molecular weight $M_w = 30-70k$), Glycerol (99 %, Aldrich chemicals), Citric Acid (Aldrich, Citric Acid, USP Anhydrous),
5 distilled water, dry ice (or solid phase CO_2), thermally insulated box.

Procedure

1. Weigh 50 ± 0.2 grams of PVA, 30 ± 0.2 grams of glycerol.
2. Mix the PVA and glycerol using the mixer set a low speed (mark 2; low sheer).
3. Add 50 ± 1 ml of water gradually to the dry mix maintaining the mechanical mix for 2
10 minutes. A smooth gel should be obtained.
4. Increase the mix speed high sheer to the maximum setting (mark 8). Add 10-20 ml of water until a PVA foam is forming. Maintain high shear mixing for 3 minutes.
5. The active ingredients, for example from 2-10 gram of enzyme, are progressively added to the foam under a maintained mechanical mixing so that a uniform active
15 foam is obtained.
6. Stop mixing. Spread the PVA foam in moulds avoiding any collapsing of the structure.
7. Place the filled moulds in a thermally insulated box 1/3 filled with dry ice. Leave to freeze for 5 hours.
8. Quickly place frozen samples in a vacuum freeze-dryer (Edward XX) for 24 hours.
- 20 9. Remove dried sample from moulds.

Any active ingredient can be added in step 5, at any level, normally up to about 50 grams, for example fabric softeners, bleaching species, nonionic surfactants.

- 25 Any stabilising agent can be added in step 5, at any level, normally up to about 50 grams, for example, bovine serum albumin, ammonium sulphate, sucrose and monostyrenated phenol.

Example 3

30

A process of making elastic articles of the invention, in the form of tablets, beads or particles

Apparatus: as described in the above example

- 5 Chemicals: Poly (vinyl alcohol) (Aldrich chemicals, molecular weight $M_w = 30-70k$), Glycerol (99 %, Aldrich chemicals), Citric Acid (Aldrich, Citric Acid, USP Anhydrous), Sodium carbonate (Aldrich, Anhydrous), Dodecyl Sulphate surfactant (Aldrich), distilled water, Petri dish (diameter 90 mm), Oven (set at $45\text{ }^{\circ}\text{C} \pm 2^{\circ}\text{C}$)

Process:

- 10 1. Weigh 50 ± 0.2 grams of PVA, 30 ± 0.2 grams of glycerol, 20 ± 0.2 grams of sodium carbonate, and 2 ± 0.2 grams of sodium dodecyl sulphate.
2. Mix the PVA, glycerol and sodium dodecyl sulphate using the mixer set a low speed (mark 2).
3. Add 50 ± 1 ml of water gradually to the dry mix maintaining the mechanical mix for 2
- 15 minutes. A smooth gel should be obtained.
4. Add the active ingredient, for example 5 gram enzyme, and sodium carbonate and mix vigorously for 30 second until a fully expanded foam is obtained
5. Spread the foam in petri dish in a uniform 1cm thick layer
6. Place petri dish in $40\text{ }^{\circ}\text{C}$ oven for 24 hours.
- 20 7. Remove the dried foam film from mould.

Any active ingredient can be added in step 4, at any level, normally up to about 50 grams, for example fabric softeners, bleaching species, nonionic surfactants.

- 25 This was repeated by using 55wt% polycarboxylic acid polymer, 20wt% anhydrous sodium carbonate and 25wt% enzyme, softening clay etc.; and repeated by using 45wt% polycarboxylic acid polymer, 15wt% polyethylene glycol, 20wt% anhydrous sodium carbonate and 20wt% enzyme, softening clay etc.

Claims

1. An elastic article comprising;
 - a) an active ingredient; and
 - 5 b) a foam matrix formed from at least one polymeric material and a plasticiser; and
 - c) a stabilising agent;whereby said article is capable of delivering said active ingredient to a liquid environment.
- 10 2. An elastic article according to claim 1, whereby said active ingredient is active in an aqueous environment, and whereby said article is water-dispersible, water-disintegrating or water-soluble, preferably water-soluble.
- 15 3. An elastic article according to any preceding claim, whereby said matrix has a glass transition temperature (T_g) of below 50°C, preferably below 40°C, and optionally between -20°C and 20°C, preferably between -10°C and 10°C.
- 20 4. An elastic article according to any preceding claim, whereby said matrix has an elastic modulus of less than 1 GN.m⁻², preferably less than 0.1 GN.m⁻², or even less than 0.01 GN.m⁻².
5. An elastic article according to any preceding claim, whereby said stabilising agent comprises a foam stabilising agent.
- 25 6. An elastic article according to any preceding claim, whereby said active ingredient is a cleaning product ingredient, fabric care ingredient, pharmaceutical ingredient or cosmetic ingredient, preferably selected from enzymes, surfactants, brighteners, dyes, suds suppressers, bleaches, bleach activators, fabric softeners, fabric conditioners, antibacterial agents, effervescence systems and mixtures thereof.

30

7. An elastic article according to any preceding claim, whereby said active ingredient comprises at least an enzyme, and whereby said stabilising agent comprises an enzyme stabilising agent, preferably said stabilising agent is an enzyme stabilising agent.

5 8. An elastic article according to any preceding claim, whereby said polymeric material comprises a water-soluble polymer, preferably a water-soluble polyvinyl alcohol.

9. An elastic article according to any preceding claim, which is in the form of a particle having a volume mean particle size of from 50 to 4000 microns, preferably from 100 to
10 1500 microns.

10. An elastic article according to any preceding claim, which has a relative density of from 0.05 to 0.9, preferably from 0.3 to 0.7.

15 11. An elastic article according to any preceding claim, whereby said matrix forms a series of closed and open cells, whereby the number ratio of closed cells to open cells is preferably at least 1:1.

12. An elastic article according to claim 7, obtainable by a process comprising the steps
20 of;

a) obtaining a mixture of a polymeric material and a plasticiser, preferably water and another plasticiser; and

b) chemically or physically introducing a gas in said mixture; and

c) prior to step b) and/or simultaneous with step b) and /or subsequent to step b),

25 contacting an active ingredient to said mixture; and

d) prior to step c) and/or simultaneous with step c) and /or subsequent to step c),

contacting a stabilising agent to said mixture; and

e) shaping the articles of the resulting mixture;

whereby preferably one or more steps a) to e) are followed or accompanied by the

30 removal of part of the water, if present.

13. An elastic article according to claim 12, whereby said active ingredient is contacted to said stabilising agent prior to said active ingredient being contacted to said mixture of polymeric material and plasticiser.
- 5 14. Use of an elastic article according to any of claims 1 to 14 to deliver active ingredients to an aqueous environment, preferably the active ingredients being detergent active ingredients, preferably enzymes, and the aqueous environment being the wash water.
- 10 15. Use of an elastic article according to any of claims 1 to 14 in cleaning compositions, fabric care compositions, personal care compositions, cosmetic compositions or pharmaceutical compositions, preferably to incorporate therein active ingredients selected from enzymes, perfumes, surfactants, brighteners, dyes, suds suppressers, bleaches, bleach activators, fabric softeners, antibacterial agents, effervescing systems, and
- 15 mixtures thereof.

INTERNATIONAL SEARCH REPORT

In International Application No

PCT/US 00/27300

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D17/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 543 439 A (MCDERMOTT KEITH J ET AL) 6 August 1996 (1996-08-06) claim 1 ---	1,2,5,6, 8,14,15
X	EP 0 334 490 A (INT FLAVORS & FRAGRANCES INC) 27 September 1989 (1989-09-27) page 9, line 44 claims 1-6 ---	1,2,6-8, 12,14,15
X	WO 98 28339 A (ALLIED COLLOIDS LTD) 2 July 1998 (1998-07-02) page 11, line 21 - line 25 page 5, line 12 -page 7, line 7 page 13, line 19 - line 22 page 8, line 16 - line 18 --- -/--	1,2,5,6, 8,9,11, 14,15

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

1 February 2001

Date of mailing of the international search report

08/02/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Richards, M

INTERNATIONAL SEARCH REPORT

In International Application No

PCT/US 00/27300

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 12291 A (SURUTZIDIS ATHANASIOS ;LEBLANC MICHAEL JUDE (US); PROCTER & GAMBLE) 26 March 1998 (1998-03-26) page 9, line 16 - line 27 page 11, line 25 - line 30 page 23, line 35 - line 36 ----	1-3,6-8, 12,14,15
X	WO 93 22417 A (UNILEVER PLC ;UNILEVER NV (NL)) 11 November 1993 (1993-11-11) page 32, line 13 - line 30 claims 1-12 ----	1,2,6-8, 12,14,15
X	FR 2 120 295 A (BALDON GUY) 18 August 1972 (1972-08-18) claims 1-5 ----	1,2,5,6, 8,14,15
X	EP 0 539 025 A (UNILEVER PLC ;UNILEVER NV (NL)) 28 April 1993 (1993-04-28) claims 1-17 ----	1,2,5,6, 8,9,14, 15
X	US 5 385 959 A (TSAUR LIANG S ET AL) 31 January 1995 (1995-01-31) column 20, line 35 - line 50 column 12, line 50 - line 52 claim 1 -----	1,2,6-9, 12,14,15

INTERNATIONAL SEARCH REPORT

Information on patent family members

In: tional Application No

PCT/US 00/27300

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5543439	A	06-08-1996	AU 679651 B	03-07-1997
			AU 4025795 A	05-09-1996
			DE 69512020 D	14-10-1999
			EP 0728804 A	28-08-1996
			ES 2136255 T	16-11-1999
			GB 2290300 A, B	20-12-1995
			NL 1001434 C	05-02-1998
			NL 1001434 A	28-08-1996
			NZ 280593 A	26-07-1996
EP 0334490	A	27-09-1989	US 4842761 A	27-06-1989
			DE 68918142 D	20-10-1994
			DE 68918142 T	12-01-1995
WO 9828339	A	02-07-1998	AU 5331798 A	17-07-1998
			AU 5331898 A	17-07-1998
			AU 5331998 A	17-07-1998
			BR 9713619 A	11-04-2000
			BR 9713634 A	11-04-2000
			EP 0950087 A	20-10-1999
			EP 0950088 A	20-10-1999
			EP 0950070 A	20-10-1999
			WO 9828396 A	02-07-1998
			WO 9828398 A	02-07-1998
			US 6024943 A	15-02-2000
			ZA 9711578 A	23-06-1999
			ZA 9711582 A	23-06-1999
			ZA 9711589 A	23-06-1999
WO 9812291	A	26-03-1998	BR 9711801 A	24-08-1999
			CA 2250324 A	26-03-1998
			CN 1213399 A	07-04-1999
			EP 0931130 A	28-07-1999
			JP 2000500822 T	25-01-2000
			US 6025319 A	15-02-2000
WO 9322417	A	11-11-1993	US 5281357 A	25-01-1994
			AU 4261393 A	29-11-1993
			DE 69303293 D	25-07-1996
			DE 69303293 T	21-11-1996
			EP 0672102 A	20-09-1995
			ES 2091001 T	16-10-1996
			JP 7506137 T	06-07-1995
			US 5281355 A	25-01-1994
			US 5385959 A	31-01-1995
			ZA 9303026 A	29-10-1994
FR 2120295	A	18-08-1972	NONE	
EP 0539025	A	28-04-1993	US 5246603 A	21-09-1993
			AU 664859 B	07-12-1995
			AU 2535792 A	01-04-1993
			CA 2078717 A, C	26-03-1993
			DE 69227883 D	28-01-1999
			DE 69227883 T	12-05-1999
			ES 2124720 T	16-02-1999
			JP 2837042 B	14-12-1998
			JP 5222672 A	31-08-1993

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/27300

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5385959 A	31-01-1995	AU 4261393 A	29-11-1993
		DE 69303293 D	25-07-1996
		DE 69303293 T	21-11-1996
		WO 9322417 A	11-11-1993
		EP 0672102 A	20-09-1995
		ES 2091001 T	16-10-1996
		JP 7506137 T	06-07-1995
		ZA 9303026 A	29-10-1994
